

Curing Behavior and Adhesion Performance of Urea-Melamine-Formaldehyde (UMF) Resin by Staged Addition of Melamine

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멜라민 첨가 순서에 따른 UMF 접착제의 경화거동과 접착력의 영향

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Abstract: The objective of this research was to investigate the curing behavior and adhesion performance of urea-melamine-formaldehyde (UMF) resin for the four types of UMF-1, UMF-2, UMF-3, and UMF-4 which synthesized by the staged addition of melamine. Also, various network structures of these resin types were discussed based on their different curing behavior and adhesion performance. The curing behavior was evaluated by DMTA and thermal stability was checked by TGA. Adhesion performance was evaluated by dry and wet shear strengths and the pH value of each cured resin was checked to see its effect on the adhesion performance. The results indicated that the UMF-1 resin type by the addition of melamine initially with the urea and formaldehyde at the same F/(U+M) rate showed the lowest thermal stability, rigidity (ΔE), temperature of $\tan \delta$ maximum ($T_{\tan \delta}$), and wet shear strength, and pH value of cured resin. In wet shear strength, however, the UMF-4 resin type appears to be slightly higher than UMF-1 resin type.

Keywords: urea melamine formaldehyde, curing behavior, resin, adhesion performance

1. Introduction

Urea-formaldehyde (UF) resin is one of the most important adhesives for interior-grade wood composite boards, such as particleboard, medium-density fiberboard, and plywood. It, however, has the disadvantages of low water resistance and high formaldehyde emission. Thus, melamine has commonly been added for improving water resistance and physical strength as well as for reducing formaldehyde emission of UF resin.

Although the chemistry of melamine-formaldehyde (MF) resin is similar to that of UF resin, MF resin optimally reacts at pH 6~9 but too fast at pH 4~5, while UF resin optimally reacts at pH 4~5 but too slow at pH 6

~9. So, adding melamine early with the first urea and formaldehyde and reacting at pH of 6~9, a common procedure used in prior research, resulted in a very high extent of polymerization between melamine and formaldehyde components and only a little extent of polymerization between urea and formaldehyde components. On the other hand, adding melamine after the UF base resin which was reacted to various different extents of polymerization, first at pH of 7~8 and then at pH of 4~5 and, after adjusting the pH to 6~9 has been advanced to a high extent and resulted in a very low extent of polymerization for MF components. Consequently, the UMF resins synthesized by the different synthesis methods showed the different chemistry and physical characteristics because of the different molecular weight distribution attained. In generally, the former called se-

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Table 1. Staged addition of melamine in UMF resin synthesis and mixing process

	UMF resin type	Step 1	Step 2	Step 3*
1	UMF-1	U1 + M1 + F1	-	-
2	UMF-2	U1 + F1	M1 + F2	-
3	UMF-3	U1 + M1 + F1	M2 + F2	-
4	UMF-4	U1 + M1 + F1	M2 + F2	M3

* Step 3 is the one mixing with catalyst and extender

Table 2. Physical and chemical properties by the type of UMF resin

	UMF resin type	F/(U+M) Molar Ratio	M/U Molar Ratio	Solids Content (wt%)	Viscosity (cPS)	pH of resin
1	UMF-1	2.26	0.45	49.21	394.7	9.60
2	UMF-2	2.26	0.45	54.46	277	9.47
3	UMF-3	2.26	0.45	51.51	192.7	9.41
4	UMF-4	2.26	0.45	49.48	164.1	9.57

quential UMF resins, while the latter called nonsequential UMF resins and the sequential UMF resins gives the good performance than nonsequential UMF resins [4].

In this relation, studies for nonsequential UMF resins and sequential UMF resins have been carried out by the aid of fourier transform infrared (FT-IR), C-NMR spectra, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA) [1-7].

In present study, the difference on the curing behavior and adhesion performance among two UMF resins synthesized by the addition of low level melamine in the first stage of the synthesis and after the synthesis was completed, which was based on sequential UMF resin synthesis methods and nonsequential UMF and sequential UMF resins at the same F/(U+M) and M/U rate was investigated through TGA, DMTA, pH value measurement of cure resin, and plywood shear strength testing.

2. Experimental

2.1. Synthesis of UMF Resin

In the present study, four types of UMF resin, UMF-1, UMF-2, UMF-3, and UMF-4, at the same F/(U + M) ratio were synthesized in the laboratory. UMF-1 resin type was synthesized by reacting the 35%~40% aqueous formaldehyde (F1), urea (U1), and melamine (M1) at an F1/(U1+M1) ratio of 2.26 and M1/U1 ratio of 0.45 in the reactor at pH of 8~9 and temperature of 80°C.

UMF-2 type was synthesized by adding melamine (M1) and the second formaldehyde (F2), attaining (F1 + F2)/(M1 + U1) of ratio of 2.2 to the base UF resin synthesized beforehand by reacting formaldehyde (F1) and urea (U1) at an F1/U1 ratio of 2.0 in accordance with the conventional alkaline-acid condition and reacting at a pH of 6.4 and a temperature of 90°C. UMF-3 type was synthesized by adding the second melamine (M2) and the second formaldehyde (F2), attaining (F1 + F2)/(M1 + M2 + U1) ratio of 2.2 to the base UMF resin synthesized beforehand by reacting formaldehyde (F1), urea (U1) and melamine (M1) at an F1/(U1+M1) ratio of 2.09 and M1/U1 ratio of 0.1 in accordance with the conventional alkaline-acid condition of the UF resin and reacting at a pH of 6.4 and a temperature of 90°C. UMF-4 resin type was made by the synthesis of UMF-3 resin [(F1 + F2)/(M1 + M2 + U1) = 2.43, F1/(U1 + M1) = 2.3] according to the above procedure, followed by the addition of the third melamine (M3) [M/U = 0.1] when was mixed with catalyst (NH₄Cl) and extender (wheat flour). The method of staged addition of melamine in UMF resin synthesis and their respective properties were shown in Tables 1 and 2, respectively.

2.2. Thermogravimetric Analysis (TGA)

All the UMF resin types cured were analyzed in nitrogen at a heating rate of 20 °C/min by a thermogravimetric analyzer. Ten milligrams of each cured sample were placed on a balance located in the furnace and

heated from room temperature to 600°C. High-purity nitrogen gas consisting of 99.5% N₂ and 0.5% O₂ was used as the inert purge gas to displace air in the pyrolysis zone in order to avoid unwanted oxidation of the sample. A constant flow was fed to the system at a rate of 20 mL/min from a point below the sample.

2.3. Dynamic Mechanical Thermal Analysis (DMTA)

The viscoelastic property of each sample was determined from 30°C to 250°C at a heating rate of 5 °C/min in a dynamic mechanical thermal analyzer (DMTA). As the resin was in a viscous liquid state, the DMTA sample was prepared by sandwiching it between two layers of wood veneer, each 0.6 mm thick, and a three-point bending mode was applied. The resin thickness was 0.2 mm, and thus the sample dimension was 40 mm long, 5 mm wide, and 1.4 mm thick. During the DMTA analysis, the frequency was maintained at 1 Hz with a strain of 0.5.

2.4. Measurement of pH Value of Cured Resin

The pH of cured resin was determined according to the ASTM D 1583-01 (American Society for Testing and Materials, 2001). For curing, the liquid resin was placed on glass plate in a circulating air oven at $66 \pm 1^\circ\text{C}$ until most of the solvent was evaporated. This usually required 4 hours. The temperature was then raised to $150 \pm 1^\circ\text{C}$ and the resin on plate was heated continuously until completely cured. This process usually required less than 1 hour.

Thereafter, the cured resin film was grounded to particle size of 425 μm . Immediately after grinding, the particles (2 g) were placed and covered with the distilled water (10 mL) in a small glass vial for the adequate immersion of an electrode. The suspension of ground particles was allowed to stand for 72 hours at room temperature. The solution was stirred and its pH was measured by a pH meter.

2.5. Plywood Shear Strength Testing

For measuring shear strength, 3-ply plywood was manufactured with veneers, the 30×30 cm in size and the moisture content of 6~10%. The adhesive was prepared by the addition of 1% ammonium chloride powder and 10% wheat flour on the basis of solid weight of resin. Spread, i.e. the amount of prepared adhesive per unit area of wood surface, was $17 \text{ g}/30 \times 30 \text{ cm}^2$. Cold

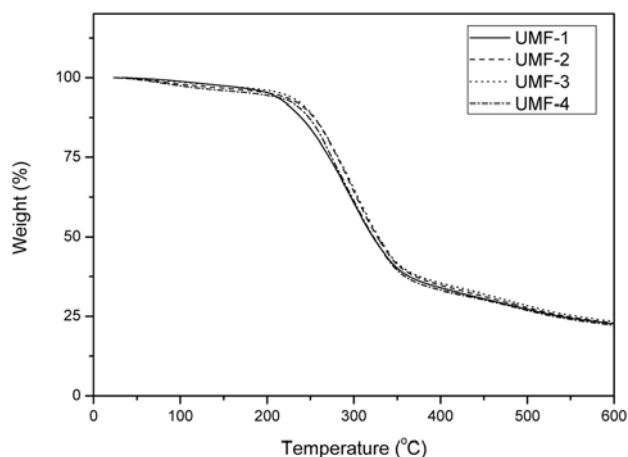


Figure 1. Weight loss curve of cured resin by the type of UMF resin.

pressing was taken for 30 min at a pressure of 1 kg/cm², followed by hot pressing at a pressure of 10 kg/cm², a temperature of 110°C, and a time of 20 sec/mm of thickness.

The shear strength test was done in conformance with the procedure of Korean Standard (KS F 3101).

3. Results and Discussion

3.1. Thermal Property by UMF Resin Type

Figure 1 shows weight loss of the cured resin by type of UMF resin from TGA analysis. Irrespective of resin type, the cured resin is slightly stable thermally up to 200°C but its weight loss increases distinctly beyond 200°C, and shows one step of active weight loss with increased temperature. This may be attributed to the fact that thermal stability characteristic of the UMF resin used in present study is nearly identical with that of UF resin with the major weight loss of UF resin at the temperature of about 220 to 280°C but not that of MF resin exhibited two steps of active weight loss with elevated temperature [13,14]. The slight weight loss at the temperature of up to 200°C may be derived from the low formaldehyde emission and from water evaporation formed by condensation reaction, while the major loss at the temperature of 200 to 400°C may be caused by the structural decomposition of the polymer [14]. The derivative thermo gravimetric (DTG) curve shown in Figure 2 is the 1st derivative of TGA curve. In the Figure 2, the thermal stability of UMF-1 resin was showed slightly lower than of the other resin types and those of the

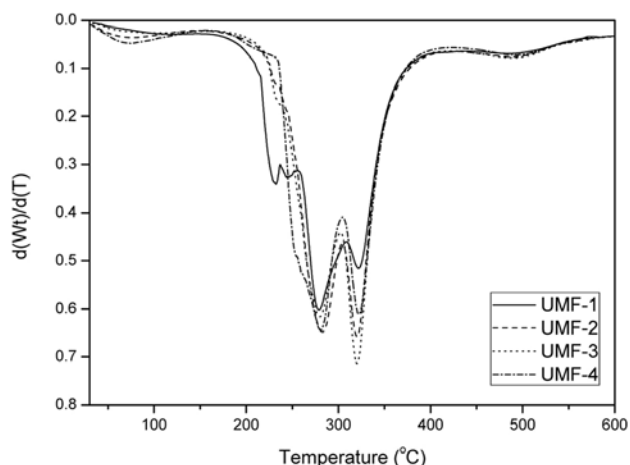


Figure 2. DTG curves of cured resin by the type of UMF resin.

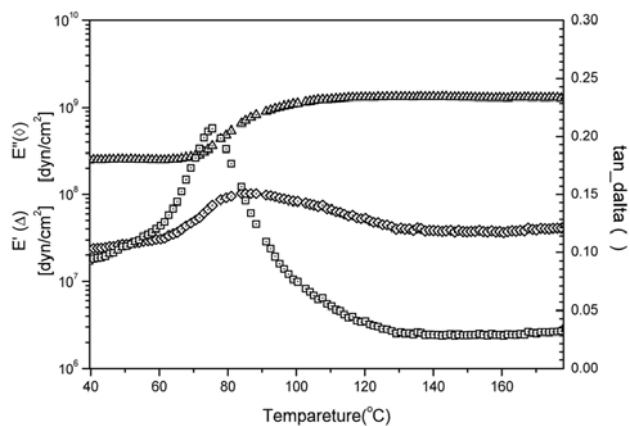


Figure 3. DMTA thermogram of the UMF-1 resin type.

other resin types were not showed the distinct difference. This may be contributed to the lower condensates of melamine formaldehyde components and urea and formaldehyde components polymerized to the lower extent in UMF-1 resin.

3.2. Viscoelastic Property by UMF Resin Type

Dynamic thermal mechanical test methods have been widely used for investigation of the structures and viscoelastic properties of thermosetting adhesives [8,11]. In present study, the variations of storage modulus (E'), loss modulus (E''), and loss factor ($\tan \delta$) of UMF resins with increasing the temperature were obtained by the aid of DMTA. Figure 3 shows DMTA thermogram of UMF-1 resin type, which is generally similar to those of the other UMF resin types. As shown in Figure 3, E' increases with the increase of temperature due to the water evaporation

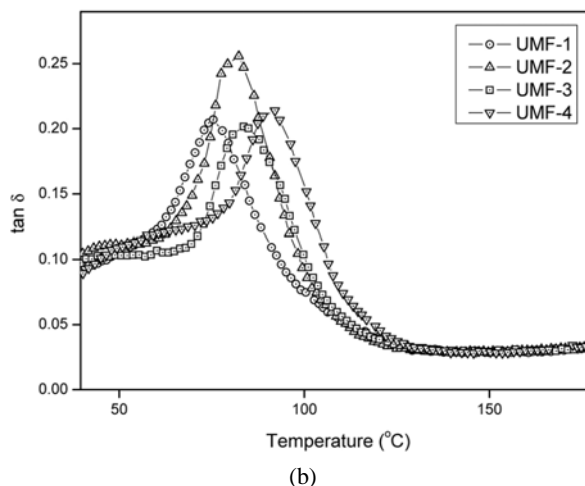
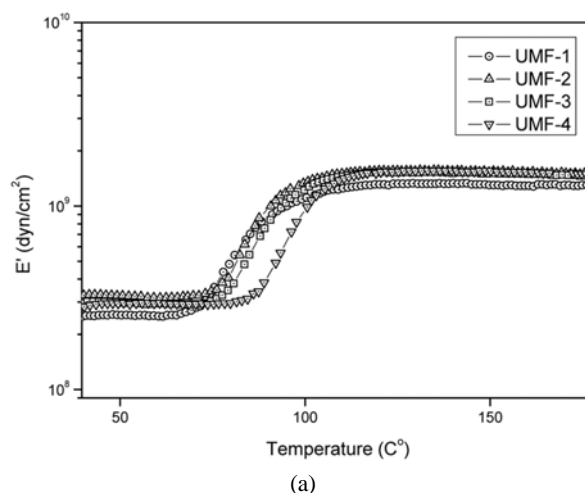


Figure 4. Storage modulus (E') and $\tan \delta$ peak by the type of UMF resin.

from the sample and the cross-linking by the curing reaction and reached a maximum value when the curing reaction was completed, and the $\tan \delta$ value increases steeply up to maximum value because of increase in viscosity and then decreased with the increase of temperature, finally slightly increased again after the curing reaction was completed [12]. The $\tan \delta$ peaks and E' of each resin type and the $\Delta E'$ used to evaluate the rigidity of the cured resin and the temperature of $\tan \delta$ maximum ($T_{\tan \delta}$) of each resin type are shown in Figures 4 and 5, respectively. In Figure 5, the $\Delta E'$ of UMF-1 resin type is the lowest but those of the other resin types were not changed significantly. In the $T_{\tan \delta}$, also, the UMF-1 resin type is the lowest and the UMF-4 resin type is the highest but the UMF-2 and UMF-3 resin type exhibited no difference. The UMF-1 resin synthesized by adding melamine initially with the

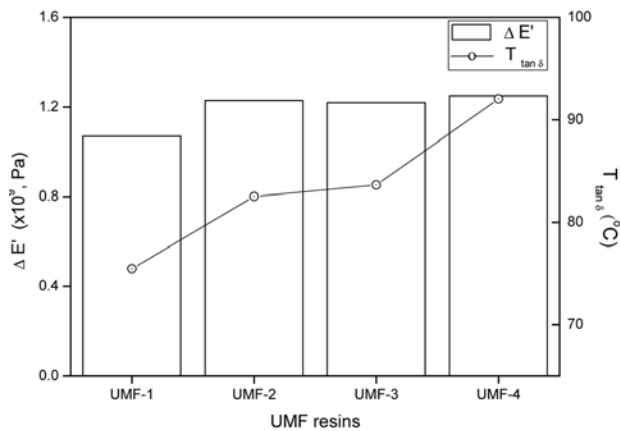


Figure 5. Rigidity ($\Delta E'$) and temperature of $\tan \delta$ maximum ($T_{\tan \delta}$) by the type of UMF resin.

urea and formaldehyde and reacting this mixture at pH 6~9 was contained a very high extent of polymerization between melamine and formaldehyde components and only a little extent of polymerization between urea and formaldehyde components due to the different reaction rate of melamine and urea with formaldehyde. In addition, the lower advancement of the UF resin components in UMF resins lengthened cure time [4]. Therefore, the cocondensates of MF resin components and UF resin components in UMF-1 resin was produced less when compared to the other resin types, thus resulting in lower $\Delta E'$. Also, UMF-1 resin type contains a very high extent of polymerization between melamine and formaldehyde components in comparison with the other resin types at the same F/(U + M) rate condition, and thus may have lower $T_{\tan \delta}$ similarly to the mixture of UF and MF resins. The temperatures corresponding to the maximum values of $T_{\tan \delta}$ decrease with the increase of MF resin ratio, i.e. in the order of UF > UF8 : MF2 > UF2 : MF5 > MF, because MF resin reacts with formaldehyde faster than UF resin in the early stage of the reaction [12]. On the other hand, higher $T_{\tan \delta}$ of UMF-4 resin type is feasible because it is cured at less acidic condition due to the addition of melamine finally in the preparation of adhesive for manufacturing plywood.

3.3. pH Value of Cured Resin and Shear Strength by UMF Resin Type

Figure 6 shows the pH value of cured resin by type. The pH value of UMF-4 resin type is the highest and this may be attributed to the addition of melamine finally after the completion of synthesis reaction. Figure 7

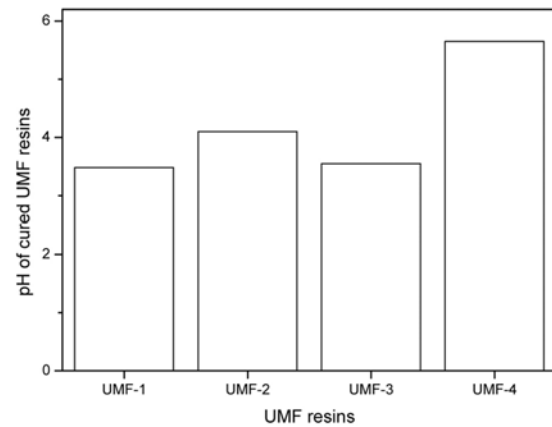


Figure 6. pH value of cured resin by the type of UMF resin.

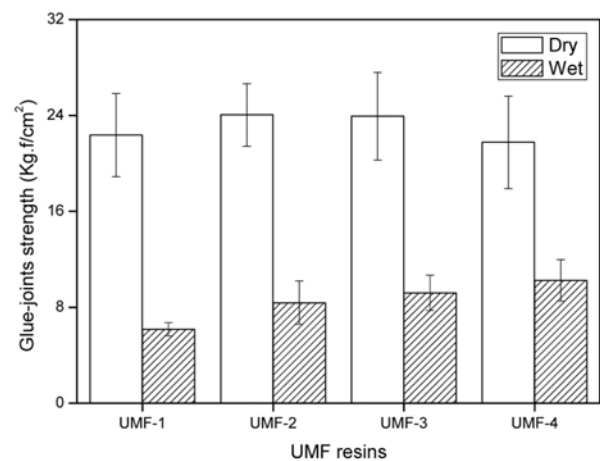


Figure 7. Dry and wet shear strengths by the type of UMF resin.

shows the dry and wet shear strength of 3-ply plywood by resin type. Irrespective of resin type, the dry shear strength does not show any distinct difference due to the same F/(M + U) and M/U rate. In wet shear strength, however, the UMF-1 resin type shows the lowest and the UMF-4 resin type appears to be slightly higher than UMF-1 resin type. The results is because the UMF-4 resin have less hydroxymethylureas as compared with UMF-1 resin due to a very high extent of polymerization between urea and formaldehyde components in the UMF-4 resin and the slight basic property of the melamine added finally in the preparation of adhesive for manufacturing plywood has the UMF-4 resin type cured at the less acidic condition. So, it causes UMF glue line to hydrolyze less, resulting in the highest wet shear strength [9].

4. Conclusions

This study was conducted to investigate the curing behavior and adhesion performance of urea-melamine-formaldehyde (UMF) resin for the four types of UMF-1, UMF-2, UMF-3, and UMF-4 which synthesized by the staged addition of melamine. In the thermal stability, the UMF-1 resin type was the lowest and other three resins were not showed the difference. And the rigidity ($\Delta E'$) and temperature of $\tan \delta$ maximum ($T_{(\tan \delta)}$) of UMF-1 resin type was the lowest but $T_{(\tan \delta)}$ of UMF-4 resin type was highest. The dry shear strength by resin type did not show any distinct difference. In the wet shear strength, the UMF-1 resin was the lowest but the UMF-4 resin was highest. Also, the pH value of cured resin was the highest in the UMF-4.

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